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# Adsorption behavior of phenanthrene onto coal-based activated carbon prepared by microwave activation

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## Abstract:

Coal-based activated carbon (CAC) was prepared from coal produced in Xinjiang of China by microwave activation. CAC was characterized and used as an adsorbent for phenanthrene adsorption. The effects of temperature, adsorption time, CAC amount, initial concentration and pH value of solution on phenanthrene adsorption were studied. The adsorption rate of phenanthrene onto CAC was obtained nearly 100% with initial concentration of 100 mg/L and CAC dosage of 0.3 g at 25 °C. Phenanthrene adsorption was well described with the Langmuir isotherm. The pseudo-second-order model was found to more effectively explain the adsorption kinetics of phenanthrene. The lower temperature was favorable to the adsorption rate and equilibrium adsorption capacity of phenanthrene onto CAC. The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  computed for phenanthrene adsorption onto CAC demonstrate the process was spontaneous, radiative, and entropically driven. Thus, CAC prepared by microwave activation could be effective for removing phenanthrene.

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20 **Key words:**

21 Coal-based activated carbon; Microwave activation; Phenanthrene; Adsorption; Kinetics and  
22 thermodynamics

23 **1. Introduction**

24 Polycyclic aromatic hydrocarbons (PAHs) can transport long distance in air and water, and are  
25 difficult to biodegrade, due to their chemical persistence and semi-volatile nature. Some PAHs are  
26 capable of interacting with DNA to promote mutagenic and carcinogenic responses. Sixteen PAHs  
27 are on the US-EPA's priority pollutants list [1]. As one of PAHs, phenanthrene is a widespread  
28 environmental pollutant and has been widely concerned due to its toxic property [2, 3]. However,  
29 phenanthrene is not efficiently removed by conventional physicochemical methods, such as  
30 coagulation, flocculation, sedimentation, filtration, or ozonation [4]. Now extensive research has  
31 been conducted using adsorption method by various sorbents to removal phenanthrene in  
32 contaminated water [5-13]. Tang et al. [9] found that the sorption performance of PAHs on fibric  
33 peat could be improved through modification by hexadecyltrimethylammonium bromide, and its  
34 equilibrium sorption capacity for phenanthrene was 854 mg/g at the phenanthrene concentration of  
35 890 mg/L and sorbent concentration of 30 mg/50 ml. Li et al. [10] reported a phenanthrene removal  
36 efficiency of 89.41-91.16% from aqueous solution by hydrolyzed pink bark. Yuan et al. [11] reported  
37 a phenanthrene removal efficiency of 95.20% for petroleum coke-derived porous carbon. Kong et al.  
38 [14] reported that the removal efficiency of phenanthrene approached 100% at a carbon  
39 concentration of 10 mg/32 ml and a carbonization temperature of 700 °C. Furthermore, with the  
40 presence of acenaphthene and naphthalene as co-contaminants, the removal efficiency of

41 phenanthrene by the prepared carbon was 99.60 %, which was comparable to that by the commercial  
42 carbon.

43 Activated carbon (AC) is one of the most commonly used adsorbent, which adsorption processes  
44 effective for the removal of persistent organic pollutants [15-18]. Activated carbons are porous  
45 material with extremely high surface area; they have been widely used in a variety of industrial  
46 applications such as separation/purification of liquids and gases, removal of toxic substances,  
47 catalysts and catalyst support, supercapacitors, electrodes and gas storage [19]. Major raw materials  
48 for the preparation of AC are coal, petroleum, peat, wood and agricultural wastes. Among which,  
49 coal is the most commonly used precursor for AC production due to the advantage of its availability  
50 and cost [19].

51 There is abundant resource of coal with geological coal reserves exceeding 2.19 million tons  
52 accounting for 40 % of China in Xinjiang (Autonomous Region, China), which has been become the  
53 large-scale coal production base [20]. Providing abundant raw materials is important for the  
54 development of high-value-added coal chemical products. For this reason, coal is selected as a stable  
55 alternative for the preparation of activated carbon in Xinjiang.

56 The CACs usually were prepared by traditional heating method by thermal conduction  
57 transferring from surface into interior of the material using the tubular furnace at relatively high  
58 temperature and long time; as a result, the process of heating was slow, high energy consumption  
59 and non-uniform with the surfaces [21]. In recent years, microwave irradiation has been widely  
60 investigated because that microwave radiation supply directly energy to carbon skeleton at molecular  
61 level from interior of the char particle to its surface to promote activation reaction more quickly and  
62 effectively at a lower bulk temperature [22]. Thus, microwave heating provides additional

advantages such as energy savings, shortening the processing time, precise control of temperature, and reduced waste comparing with traditional heating techniques. So coal-based activated carbon would be prepared by microwave activation was considerably informative and significant. And exploring the adsorption behavior of phenanthrene onto CAC obtained by microwave activation from 30% ethanol aqueous solution is quite interesting and innovative. In addition, 30 vol. % ethanol was added to the solution for enhancing the water solubility of phenanthrene.

This paper was attempted to study the sorption characteristics of phenanthrene on CAC by changing temperature, time, CAC amount, initial concentration and pH of phenanthrene solution. To better understand these adsorption processes, equilibrium adsorption data were used in kinetics and mass transfer models in this study. These models were proposed to predict the adsorption behavior and the mechanisms, providing a foundation for developing CAC products as potential adsorbent to remove PAHs in the environment.

## **2. Materials and methods**

### **2.1. Materials**

The raw anthracite coal was purchased from TBEA, Changji, Xinjiang Uygur Autonomous Region, China. The resultant coal sample passed through a 100 mesh sieve was used to prepare the CAC. Phenanthrene (>97 %; Aladdin, Shanghai, China) was used to prepare the stock solutions by dissolving an appropriate amount in ethanol aqueous solution.

### **2.2. Preparation and analyses of CAC**

CAC was prepared with a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45 GHz. The oven was equipped with a power controller and a timer controller. The solid KOH (15 g) and dried coal mixture with a ratio of 1:3 was placed in a quartzose tube of a microwave reactor to

85 activate under vacuum atmosphere at a 693 W for 10 min. The AC samples obtained repeatedly was  
86 washed with 10 % hydrochloric acid and then with distilled water until the filtrate reached neutral.  
87 The remaining solid was dried in an oven at 110 °C for 4 h and stored in sealed glass bottles for the  
88 adsorption experiments.

89 Elemental analysis of CAC was carried out by elemental analyzer (VARIO ELIII, Elementar  
90 Analysensysteme GmbH). The pore structure of CAC was evaluated by measuring nitrogen  
91 adsorption isotherm at 77 K with ASAP 2020C surface area and porosity analyzer (Micromeritics  
92 Instrument Corp, USA). The  $S_{\text{BET}}$  was calculated using the BET equation.

93 The study of surface acidity of CAC was implemented by mixing 0.20 g of CAC with 25.00 ml  
94 of 0.05 M NaOH and agitating for 48 h at  $30 \pm 1$  °C, then the suspension containing remained NaOH  
95 was titrated with 0.05 M HCl. The surface basicity of CAC was measured by titration with 0.05 M  
96 NaOH after shaking mixture which containing 0.20 g of CAC and 25.00 ml of 0.05 M HCl.

97 The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of porous carbon was determined according to the procedure  
98 described by Noh and Schwartz [23]. The determination process was repeated for initial pH values  
99 between 2 and 12. The final pH value was plotted against the initial pH value. The point where the  
100  $\text{pH}_{\text{final}}$  vs.  $\text{pH}_{\text{initial}}$  curve crosses the  $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$  line is the  $\text{pH}_{\text{PZC}}$ .

101 The “Boehm titration” is a commonly used technique to determine the acidic oxygen surface  
102 functional groups on carbon samples whereby bases of various strengths ( $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , NaOH)  
103 neutralize different acidic oxygen surface functionalities [24]. The weakest base,  $\text{NaHCO}_3$ ,  
104 neutralizes only the strongest acidic carbon surface functionalities (CSFs) which are carboxylic  
105 groups, while  $\text{Na}_2\text{CO}_3$  neutralizes carboxylic and lactonic groups. The strongest base typically used,  
106 NaOH, neutralizes carboxylic, lactonic and phenolic groups. The number of each type of CSF can be

determined by difference between the adsorption of each reaction base [24]. A mixture of 1.5 g CAC and 25.00 ml of one of the three 0.05 M reaction bases, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaOH was filtered and wash with distilled water adequately after stirring for 24 h, then all the filtrate collected was added 0.05 M HCl to completely neutralize and end with methyl red indicator.

### 2.3. Preparation and determination of phenanthrene stock solution

Phenanthrene was initially solved into 30 vol. % ethanol aqueous solutions to prepare the stock solutions of the given concentrations. Five initial solutions ranging from 100 to 900 mg/L were prepared. The concentrations of various phenanthrene solutions were measured after adsorption by a UV-vis spectrophotometer (UV-752N, Shanghai Metash Instruments Co., Ltd, China). The phenanthrene absorbance at 249 nm could be converted to phenanthrene concentration using the calibration curve,  $C = 3.4483A_{249} + 0.0103$ , and  $R^2$  was equal to 0.9998.

### 2.4. Adsorption experiments

#### 2.4.1. Adsorption performance analysis

For each experiment, 40 ml of phenanthrene solution of known initial concentration was placed in a 100 ml conical flask with cover. To establish the thermal equilibrium before adsorption, the solution was periodically shaken at a certain speed and constant temperature. After preheating for 5 min, 100 mg of CAC (size  $\leq 100$  mesh) was added to the solution. Then, the samples were periodically withdrawn and filtrated immediately with suction for solid-liquid separation. The supernatant solution was analyzed for the remaining concentration of phenanthrene by a UV-vis spectrophotometer.

The amount of phenanthrene ( $Q_e$ ) was calculated as follow:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$



129 The adsorption rate of phenanthrene ( $\eta$ ) was calculated as follow:

130 
$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

131 where  $C_0$  (mg/L) and  $C_e$  (mg/L) are liquid-phase concentrations of phenanthrene at initial and  
132 equilibrium, respectively.  $V$  (ml) represents the volume of the solution and  $m$  (g) stands for the mass  
133 of CAC used.

#### 134 2.4.2. Adsorption isotherm

135 The Langmuir adsorption Eq. (3), predicts the existence of monolayer coverage of the adsorbate  
136 at the outer surface of the adsorbent [25].

137 
$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

138 Where  $C_e$  and  $Q_e$  are as defined in Eq. (1),  $q_m$  is adsorption maximum (mg/g);  $K_L$  is sorption  
139 equilibrium constant (L/mg).

140 The Freundlich isotherm [25] is an empirical equation employed to describe heterogeneous  
141 systems, and is expressed by the following Eq. (4):

142 
$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \quad (4)$$

143 where  $K_F$  is a constant which represents a measure of the adsorption capacity of the adsorbent for  
144 specific solute, and  $n$  is a measure of intensity of adsorption.

#### 145 2.4.3. Adsorption kinetics

146 Kinetic models are used to examine the rate of the adsorption process and potential rate  
147 determining step, i.e., particle diffusion or chemical reaction. The capability of pseudo-first-order,  
148 pseudo-second-order and intraparticle diffusion, were examined in this study.

149 The pseudo-first-order kinetic rate equation is expressed as [26]:

$$\frac{1}{Q_t} = \frac{1}{Q_e} + \frac{k_1}{Q_e t} \quad (5)$$

where  $k_1$  is the rate constant of pseudo-first-order sorption (min). The first-order rate constant can be determined from the slope of the linearized pseudo-first-order rate equation.

The pseudo-second-order kinetic rate equation is expressed as [27]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

where  $k_2$  is the rate constant of pseudo-second-order sorption (g/mg/min). The second-order rate constant can be determined from the intercept of the linearized pseudo-second-order rate equation.

In the intraparticle diffusion model, the relationship between the adsorption capacity ( $Q_t$ ) at time  $t$ , could be written as [28]:

$$Q_t = K_p t^{1/2} + C \quad (7)$$

where  $K_p$  is the intraparticle diffusion constant (mg/g/min<sup>1/2</sup>) and  $C$  is the intercept of the line, which is proportional to the boundary layer thickness.

#### 2.4.4. Thermodynamic parameters

The activation energy,  $E_a$ , is obtained from an Arrhenius equation (8) [29]:

$$\ln(k) = \ln(A) - \frac{E_a}{R} \left( \frac{1}{T} \right) \quad (8)$$

where  $A$  the frequency factor or the Arrhenius constant,  $R$  the universal gas constant (8.314 J/K mol),  $T$  the absolute temperature, and  $k$  the rate constant, is given by the pseudo-second-order rate constant  $k_2$ .

The data obtained from adsorption isotherm models can be conveniently used to determine, such thermodynamic parameters as free energy of adsorption  $\Delta G^\circ$ , enthalpy change of adsorption  $\Delta H^\circ$  and the change in standard entropy  $\Delta S^\circ$ . These parameters are evaluated using the following equation:

$$K_d = K_F = X \quad (9)$$

where  $K_d$  (L/mol) is the sorption distribution coefficient. The  $K_d$  values were plugged into Eq. (9) to determine the free energy of sorption process at various temperatures [26].

$$\Delta G^\circ = -RT \ln K_F \quad (10)$$

Where  $\Delta G^\circ$  is the free energy of sorption (kJ/ mol). Enthalpy change  $\Delta H^\circ$  and entropy change  $\Delta S^\circ$  values were calculated at different temperatures by the following Eq. (10) [26]:

$$\ln K_F = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where  $K_F$  is the adsorption equilibrium constant in Eq. (4) for the phenanthrene.

### 3. Results and discussion

#### 3.1. Characterization of coal and CAC

The results of the analytical function of coal were as follows: 60.97% of C, 3.70% of H, 0.61% of N, and 1.53% of S, 27.51% of O, 5.68% of other element. Table 1 shows the properties of CAC. The BET surface area, total pore volume, and average pore size of CAC were 1770.49 m<sup>2</sup>/g, 0.99 cm<sup>3</sup>/g, and 2.820 nm, respectively. The CAC was suggested to have considerable surface area and total pore volume, which can make an important contribution to the adsorption capability. As listed in Table 1, microwave heating technique has shown better effect in terms of porous structure, relatively greater surface area than conventional heating method. In addition, the treatment time and the consumption of gases used in the microwave heating treatment can be considerably reduced, which resulted in a reduction in the energy consumption, compared with conventional surface heating treatment. Hence, the work clearly demonstrates that the use of microwave heating for preparation CAC is important in aspects of economic and performance. Surface acidity and basicity was a major criterion describing the surface chemistry of an adsorbent. Data analysis showed that

CAC exhibited an alkali character with surface acidity and basicity of 0.75 and 1.50 mmol/g, respectively. The alkali nature of CAC is attributed to KOH as activation agent for the CAC preparation. However, the surface acidity was associated with a low content because of the presence of oxygen-containing groups on the carbon surface, such as carboxylic groups, lactonic groups, and phenolic groups. In addition the  $pH_{PZC}$  of CAC was 8.06. The surface total acidic groups, carboxylic groups, and phenolic groups of CAC obtained by Boehm titration were 0.17, 0.07, and 0.10 mmol/g, respectively. These results also proved that CAC exhibited an alkali character.

### **3.2. Effects of conditions on adsorption behavior**

#### **3.2.1. Effects of temperature on the adsorption rate**

A series of 100 ml conical flasks with cover were set in a water bath and shaken at 90 rpm at 25, 35, 45, and 55 °C, respectively. 0.1 g of CAC was added to 40 ml of phenanthrene solution with an initial concentration of 500 mg/L. The pH value of the initial solution was 7.0. The effects of temperature on the adsorption rate were studied.

**Fig. 1** shows the variation of adsorption rate of phenanthrene with temperature. The equilibrium adsorption rate of phenanthrene on the CAC surface decreased slightly when the temperature increased. Low temperature is favorable to the adsorption rate of phenanthrene, the adsorption process of phenanthrene approached equilibrium gradually after 40 min i.e. The CAC achieved saturated adsorption after 40 min at each temperature.

**Fig. 1** shows the two stages of sorption process. In the first stage, phenanthrene was rapidly adsorbed onto those easily accessible hydrophobic sites within the CAC matrix in 20 min. The adsorption process could be the chemical interaction between phenanthrene and CAC surface. In the second stage, the adsorption was probably limited by the slow migration of phenanthrene to less

215 accessible sites associated with micropores within the CAC matrix, which could take hours.  
216 Valderrama et al. [6] reported similarly that the adsorption process of polyaromatic hydrocarbons  
217 onto granular activated carbon and Macronet hyper-cross-linked polymers (MN200) also were the  
218 two-stage. The first step of solution/solid transfer is assumed to be rapid in comparison to the  
219 intraparticle diffusion process, which is the last step of the sorption corresponding to the extraction  
220 of PAHs. And the solution film is the determining step of the mass transfer rate. Thus, 35 °C and 50  
221 min were selected as sufficient adsorption equilibrium conditions in this experiment.

### 222 3.2.2. Effects of the amount of CAC on adsorption rate and amounts

223 **Fig. 2** shows that an increase in the CAC amount resulted in an increased phenanthrene  
224 adsorption rate onto CAC. When the amount of CAC is over 0.3 g, the adsorption rate of  
225 phenanthrene slightly increase and it reached over 98% in 40 ml of solutions. This result shows that  
226 when the adsorption process is close to equilibrium, the increase of the amount of CAC has little  
227 significance. The increase in CAC amount results in the increase in the surface area of adsorption  
228 and increase in the number of adsorption sites. Gong et al. [15], who investigated the effect of  
229 activated carbon amount on PAHs removal from four oils, observed similar results and explanation.  
230 An increase in the activated carbon amount was observed to result in an increased PAHs adsorption  
231 rate on activated carbon. More than 90% of PAHs in 40 ml of oils was removed when the activated  
232 carbon amount was >3 g for oils A-C.

233 Unit adsorption amount decreased and the utilization of CAC reduced with the increase of the  
234 amount of CAC could be seen in **Fig. 2**. Given the adsorption efficiency and cost, 0.3 g was selected  
235 as the amount of CAC in this experiment.

### 236 3.2.3. Effects of the initial concentration of phenanthrene on adsorption rate and amounts

Effects of various initial phenanthrene concentrations ranging from 100 to 900 mg/L in ethanol aqueous solution on adsorption were investigated at different temperatures. As shown in Fig. 3A as the initial concentration increased, the adsorption rates showed a downward trend at the experimental temperatures. For the same initial concentration, the increase in temperature resulted in the slight decline in adsorption rate. Therefore, low temperature was more conducive to adsorption. Fig. 3B shows that an increase of adsorption amounts was observed as the initial concentration of phenanthrene increased. This result is attributed to the increased number of available sorption sites by increasing the sorbent concentration, which allows more phenanthrene molecules to pass from the bulk solution to the particle surface. [14]

#### 3.2.4. Effects of pH value

The effect of initial pH value of solution was studied under an initial phenanthrene concentration of 500 mg/L (Fig. 4). The adsorption amounts of phenanthrene with the pH values of 2, 4, 6, 7, 8, 10, 12 were 97.15, 93.59, 92.36, 93.80, 93.54, 93.98, 93.57%, respectively. The results showed that the amounts of phenanthrene adsorbed onto CAC did not change significantly when the solution value was raised from 2 to 12. Foo et al. [24] reported an enhancement of the adsorption of MB by increasing pH value from 2 to 12, and the adsorption capacity of PAC prepared via microwave assisted KOH activation increased from 321.33 to 462.77 mg/g, and that of PAC prepared via microwave assisted  $K_2CO_3$  activation increased from 257.07 to 388.58 mg/g, respectively. However, the effect of pH value on the adsorption of phenanthrene by CAC can't be observed.

### 3.3. Adsorption isotherm

The adsorption rate of phenanthrene as a function of concentration at equilibrium at various

temperatures as seen in Fig. 5. And the analysis of the isotherm data could be important and useful in the design of adsorption process equipment. Thus, the equilibrium data for adsorption of phenanthrene onto CAC were analyzed using two isotherm equations, namely, Langmuir and Freundlich. The isotherm data were fitted to the non-linearized Langmuir and linearized Freundlich models to determine the adsorption capacity (mg/g) and sorption equilibrium constants (L/mg;  $q_m$  and  $K_L$ ) and intensity parameters ( $K_F$  and  $n$ ). Table 2 shows that the Langmuir model yielded a better fit than the Freundlich model of phenanthrene adsorption with various temperatures, and these correlation coefficients ( $R^2$ ) were  $>0.9940$ , which could be due to phenanthrene monolayer adsorb onto CAC. These correlation coefficients ( $R^2$ ) obtained from the Freundlich model of phenanthrene adsorption were  $>0.9477$ . Existing studies reported that some PAHs sorption to heterogeneous carbonaceous matters gave linear isotherms. Yuan et al. [11] found that phenanthrene adsorption onto all four carbons follows the Freundlich equation to some degree, with all correlation coefficients being greater than 0.94. Gong et al. [15] also found that adsorption equilibrium of PAHs onto activated carbon from vegetable oil was successfully evaluated by the Freundlich isotherms, with all coefficients being greater than 0.93.

As shown in Table 2,  $q_m$  and  $K_L$  of phenanthrene on CAC decreased with increasing temperature indicating the lower temperature is favorable to create more adsorption sites onto CAC. The maximum  $q_m$  was 102.04 mg/g at 25 °C. The observed decrease in  $K_F$  value with increasing temperature, also implying the above-mentioned viewpoint. The values of  $n$  did not significantly change among the four temperatures due to the same carbon.

### 3.4. Adsorption kinetics

Fig. 6 shows the variation of adsorption amounts of phenanthrene with time and temperatures at

the initial concentration of 500 mg/L of phenanthrene. The results showed that the increase in temperature resulted in the change in the equilibrium time of phenanthrene in the solution adsorbed onto CAC. The enhancement of the adsorption amount was favored slightly at lower temperature. The adsorption process consisted of two distinguished periods, which agrees well with that of the aforementioned finding.

The phenanthrene adsorption onto CAC was fitted by three kinetic models, and values of  $k_1$ ,  $k_2$ ,  $k_p$ , and  $Q_e$  as well as correlation coefficients are listed in Table 3. The results showed that the correlation coefficient for the first-order kinetic model was lower than the second-order kinetic, but the theoretical  $Q_e$  values found in this model were reasonable from 25 °C to 55 °C. The experimental date of the pseudo-second-order kinetic model of phenanthrene indicated extremely high correlation coefficient ( $R^2 > 0.9998$ ) at all experimental temperatures. The theoretical  $Q_e$  values computed from this model were consistent with the experimental  $q_{exp}$  values, which suggest that the adsorption process could involve physical adsorption and a chemical interaction of valency forces by sharing of or exchange with proton between phenanthrene and CAC. The adsorption mechanism and the potential rate-determining steps could be involved in mass transport and chemical reaction processes [32].

In addition, the correlation coefficient  $R^2$  of intraparticle diffusion kinetic models was decreased up to 0.7097. Weber and Morris [29] reported that if intraparticle diffusion is involved in the sorption process, a plot of the square root of time versus adsorption would result in a linear relationship, and the particle diffusion would be the determining step if this line passes through the origin. In this study, the  $Q_t$  versus  $t^{0.5}$  graph is initially linear, indicating that intraparticle diffusion could be involved in the sorption process of phenanthrene on CAC. However, it was not the only



rate-determining step.

### 3.5. Adsorption thermodynamic properties

When  $\ln k$  is plotted versus the reciprocal of the temperature ( $1/T$ ), the slope is  $E_a$  (Fig. 7). Activation energy for the phenanthrene sorption on CAC was 23.77 kJ/mol which indicates that the main adsorption process is physical adsorption. Subsequently,  $\ln K_F$  is plotted against temperature ( $1/T$ ), as show in Fig. 8, the results of the thermodynamic parameters were evaluated for the sorption system of phenanthrene at 25, 35, 45, and 55 °C (Table 4). The negative value of  $\Delta G^\circ$  indicates the spontaneous phenanthrene adsorption onto CAC. The  $\Delta G^\circ$  values decreased lightly with increasing the temperature, indicating that the affinity between phenanthrene and CAC surface weakened with increasing temperature. This result shows that the removal process was favored at lower temperature. The negative value of  $\Delta H^\circ$  indicates an exothermal adsorption process, which is in agreement with the aforementioned result, i.e., the phenanthrene amount decreased with increasing temperature. Phenanthrene adsorption onto CAC was clearly entropically driven. The positive values of  $\Delta S^\circ$  suggest increased randomness at the solution interface during the phenanthrene adsorption processes [26].

## 4. Conclusions

The CAC prepared by microwave activation can substantially remove phenanthrene from 30 vol. % ethanol aqueous solution. The increase of the amount of activated carbon resulted in the increase in the adsorption rate and decrease in unit adsorption amount. The adsorption rate decreases and adsorption amount increases as the initial concentration increases. The pH value of solution do not affect the adsorption rate and amount of phenanthrene on CAC.

Phenanthrene adsorption was described well by the Langmuir model, and the correlation

coefficients ( $R^2$ ) were  $>0.9954$ . The lower temperature is favorable to phenanthrene adsorption onto CAC was favored at lower temperature. The kinetic of phenanthrene adsorption was described by the pseudo-second-order equation with extremely high correlation coefficient ( $R^2 > 0.9998$ ) and suggested that the adsorption involved chemical interaction. Phenanthrene adsorption onto CAC was a two-stage process.

The activation energy values indicated that the overall adsorption process of phenanthrene was physical adsorption. The thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  were computed. The phenanthrene sorption on CAC was spontaneous, radiative, and entropically driven.

This paper lays the foundation on developing CAC products with specific performance and using CAC to remove PAHs in the environment. Overall, CAC from Xinjiang region coal prepared by microwave activation could be effectively applied in liquid-phase adsorption involving PAHs.

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